

# Improved Separation in Gas Chromatography by Temperature Programming

## Application to Mercaptans and Sulfides

JAMES H. SULLIVAN,<sup>1</sup> JOHN T. WALSH, and CHARLES MERRITT, Jr.

Pioneering Research Division, Quartermaster Research and Engineering Center, U. S. Army, Natick, Mass.

► Elegant linear temperature programming combined with constant gas flow is not necessary for the separation of a mixture having a wide range of boiling points. A method of nonlinear programming is described which provides adequate separations. Conventional gas chromatography equipment may be employed with only minor modifications. The separation of a mixture of 12 mercaptans, boiling range 35° to 220° C., and a mixture of 11 sulfides, boiling range 37° to 235° C., is described. All of these compounds, including isomeric as well as normal members of each series, are efficiently separated in 28 minutes on a 7-foot squalane column which is temperature programmed from 20° to 150° C.

THE advantages of programmed temperature gas chromatography for the improved separation of mixtures of volatile components having a wide range of boiling points have been described recently (4, 7). This technique has been investigated for the separation of homologous series of aliphatic mercaptans and sulfides. Chemical methods for the separation and identification of these compounds are difficult because of the similarity of their chemical properties (9). Previous reports of the gas chromatographic separation of these volatile sulfur compounds have included only a few low molecular weight members of the series (1, 11, 12).

In many applications gas chromatography is employed primarily as a means of separation of mixtures, but to collect the individual components of the mixture it is necessary to achieve wider peak separation than is ordinarily required for analytical gas chromatography.

These studies have confirmed observations (4, 7) that improved separation is obtained when the temperature is gradually increased during the time of elution of the components of the mixture from the column. Also, good separation can

be achieved by raising the temperature in a nonlinear rather than in a linear manner. The technique permits the separation of isomeric as well as normal members of a homologous series.

### EXPERIMENTAL

**Materials and Apparatus.** The apparatus used to obtain the chromatograms was a modified Aerograph Model No. A-100 (Wilkins Instrument and Research, Inc.). Preliminary studies of temperature programming showed that considerable drift of base line resulted when the detector was heated simultaneously with the column. To eliminate this drift, the thermal conductivity cell of the Aerograph was replaced by a Gow-Mac Instrument Co. unit located outside the column oven about 8 inches from the exit end of the column. The Gow-Mac cell, containing four tungsten wire filaments having so-called TE geometry and mounted with mechanical seals, was fitted with a heater and its temperature maintained at 150° C. The tubing which connected the column and detector unit was wrapped with heater tape and also maintained at 150° C. The helium stream to the reference side of the detector was maintained at 150° C. in the same manner. In this way the gas streams flowing through the detector were always at constant temperature, thus reducing base-line drift to a minimum.

The serum cap sample inlet of the Aerograph was removed and replaced by a Fisher-Gulf capillary pipet sample introduction unit to permit introduction of reproducible volumes of sample. A separate heater for this unit ensured complete volatilization of the sample. The temperature of the inlet was also maintained at 150° C.

The bridge output signal from the detector was applied without attenuation to a Brown 0- to 10-mv. potentiometric recorder. Sample size was selected to permit all peaks to appear on scale while recording at maximum sensitivity.

The column used throughout the study was a 7-foot, 0.25-inch outer diameter stainless steel coiled column packed with 25% by weight of squalane on 30- to 60-mesh firebrick. The squalane was heated in an open oven at 135° C. for 24 hours before absorption

on the firebrick to remove lower boiling impurities. The column was mounted in the oven of the Aerograph.

The choice of squalane as the stationary phase was based on preliminary studies in this laboratory to select the most suitable column packing to permit purification of mercaptans and sulfides. In this work 18 mercaptans and 17 sulfides were screened as individuals on five stationary phases on firebrick. These were paraffin (average carbon number, C<sub>29</sub>), silicone, dinonyl phthalate, Carbowax 1500, and squalane. The best separation was obtained on squalane and paraffin. Silicone, dinonyl phthalate, and Carbowax were less satisfactory, and for higher molecular weight sulfur compounds dinonyl phthalate and Carbowax gave peaks at temperatures near the boiling points of the compounds which were rated from fair to poor.

For the separation of mixtures approximately equimolar amounts of 12 mercaptans and 11 sulfides were taken to prepare the wide boiling range mixtures of each type of compound. Somewhat larger amounts of the higher molecular weight compounds were taken to compensate for the reduced sensitivity of the detector toward these compounds and to provide peak heights of sufficient size to aid in the evaluation of the separations obtained. The compounds used and their boiling points are given in Table I. These compounds were used without prior purification, as the presence of small amounts of impurities had no observable effect on the separation of the principal components. Each mixture had a boiling point range of about 200° C. All the components were liquids and each sample was admitted to the chromatographic column through the heated Fisher-Gulf liquid inlet from a calibrated capillary pipet.

In all the studies helium was used as a carrier gas at the same initial flow rate of 100 ml. per minute. In the programmed temperature separations small decreases in flow rate (about 10 ml. per minute) were observed at the end of the run as the temperature reached its upper limit, but they did not appear to affect the separations obtained.

<sup>1</sup> Present address, McCormick and Co., Inc., Baltimore 2, Md.

Isothermal chromatograms were obtained in the conventional manner with the column maintained at a predetermined constant temperature within the oven of the Aerograph.

**Procedure.** The variable voltage transformer used to control the Aerograph oven temperature is turned up to full scale with the power switch in off-position. At the start of the run the oven is at ambient temperature (20° C.) or preheated to about 20° C. if necessary. The sample is admitted and the oven power switch is turned to on. The temperature rise characteristic of the oven under these conditions shows a slow temperature rise during the first 10 minutes after the start. The temperature then starts to rise rapidly at an increasing rate, reaching 150° C. after about 30 minutes' total elapsed time.

The nonlinear temperature characteristic thus obtained by this simple manipulation of the usual type of temperature controls is ideally suited to efficient programmed temperature gas chromatography. Data obtained using this procedure showed that the time-temperature characteristic can be easily reproduced (Table II).

Any programmed temperature rise can be obtained by manual adjustment of the variable heater voltage control during the run and the linearly programmed runs were obtained in this manner. To obtain a faster rise than that provided by the oven heater alone, an auxiliary heater can be installed in the oven.

## RESULTS AND DISCUSSION

The effect of temperature on retention volume and on separation factors has been discussed by Phillips (10) and others (5, 8). It is difficult to separate widely boiling mixtures at a constant temperature. From a series of isothermal chromatograms at 40° C. only five sulfides, boiling range 37° to 117° C., are eluted from the column and are well separated. At 80° C. eight sulfides, boiling range 37° to 165° C., may be eluted, but the lower boiling components of the mixture show poorer resolution. At 120° C. 10 of the 11 sulfides may be eluted, but some of the lower members are unresolved and the higher members show distorted peak forms. Good resolution is obtained only for those components having boiling points in the range 140° to 190° C. Similarly, at 150° C., although all the components are eluted, resolution is obtained only for components boiling in the range 180° to 240° C.

Although various devices and techniques have been employed to improve the separation of widely boiling mixtures, all suffer certain disadvantages.

Table I. Times and Temperatures of Elution for Programmed Temperature Separation

Mercaptans			Sulfides		
Compound	Boiling point, ° C.	Time, minutes	Compound	Boiling point, ° C.	Time, minutes
Ethyl	35.0	1.2	Dimethyl	37.3	1.4
Isopropyl	52.6	1.8	Methylethyl	66.7	3.3
<i>n</i> -Propyl	67.6	3.0	Methylisopropyl	84.8	4.8
Isobutyl	88.7	5.0	Diethyl	92.1	5.7
<i>n</i> -Butyl	98.5	6.6	Ethyl- <i>n</i> -propyl	118.5	9.2
Isoamyl	117-119	9.4	Di- <i>n</i> -propyl	142-144	12.9
<i>n</i> -Amyl	126.6	11.0	Isopropyl- <i>n</i> -butyl	163-165	14.2
<i>n</i> -Hexyl	149-152	15.4	Diisobutyl	170	16.0
<i>n</i> -Heptyl	174-176	16.4	Di- <i>n</i> -butyl	188	19.7
<i>tert</i> -Octyl	190-195	19.8	Diisoamyl	216	24.9
<i>n</i> -Octyl	201-203	24.3	Di- <i>n</i> -Amyl	235	28.2
<i>n</i> -Nonyl	220	29.3			

Table II. Reproducibility of Time-Temperature Program

Time	Run No.					
	1	2	$\delta^a$	3	4	$\delta^b$
Start	20° C.	20° C.	...	40° C.	40° C.	...
2	21	20	0.5	51	50	0.5
4	25	25	0	62	60	1.0
6	31	31	0	72	70	1.0
8	37	37	0	80	78	1.0
10	46	46	0	90	88	1.0
12	58	58	0	96	95	0.5
14	74	73	0.5	102	103	0.5
16	88	87	0.5	110	108	1.0
18	104	104	0	118	116	1.0
20	117	118	0.5	123	122	0.5
22	124	122	1.0	130	128	1.0
24	130	130	0	133	132	0.5
26	137	138	0.5	139	138	0.5
28	145	145	0	145	146	0.5
30	151	151	0	151	151	0

<sup>a</sup>  $\delta_{20-150^\circ \text{C.}} = 0.23$ .

<sup>b</sup>  $\delta_{40-150^\circ \text{C.}} = 0.7$ .

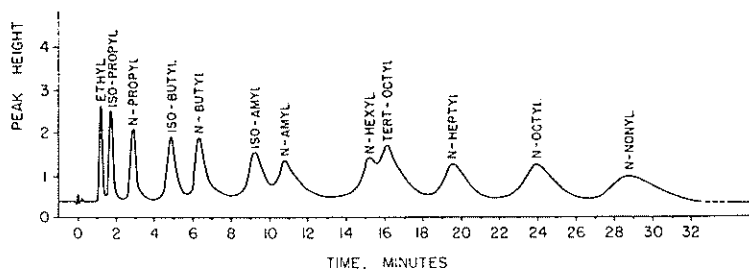


Figure 1. Nonlinear temperature programmed separation of a homologous series of mercaptans

The use of multistage columns (3) at various temperatures involves additional manipulation of the sample and extra equipment expense. The technique of raising the temperature in a stepwise manner (2, 6) during the course of elution from the column or making replicate analyses at different temperatures (8) only partially improves the separation. The conditions for optimum separation are fulfilled when the column temperature is gradually increased. If a linearly programmed temperature rise is employed, elegant

temperature and flow controllers must be incorporated in the apparatus (4). However, improved adequate separation of all members is achieved more conveniently by nonlinear programming with neither elaborate electromechanical temperature controllers nor flow controllers.

Nonlinearly programmed chromatograms of both the mercaptan series and the sulfide series are shown in Figures 1 and 2. Excellent separations were achieved for all components of each mixture and not more than 30 minutes

were required to complete the elutions. A summary of the retention times and temperatures at which the components are eluted is given in Table I. Several nonlinearly programmed temperature runs were made of both the mercaptan and sulfide mixtures and in every instance good separations were obtained.

Without rigid control of the flow rate a nonlinear program gave better separations than a linear program. Figure 3 shows a linearly programmed chromatogram of the mixture of mercaptans. The temperature rise is 7° C. per minute, which causes the lower boiling components to be eluted without sufficient separation. Figure 4 shows a chromatogram of the same mixture programmed linearly with a temperature rise of 3° C. per minute. Although the lower members of the series are all resolved, the higher members do not peak well and an excessively long time is required to completely elute all of the components. In this run the last member of the series, *n*-nonyl mercaptan, has not been eluted even after 40 minutes.

Although better linearly programmed separations can be achieved by the more elegant method of linear temperature programming with constant gas flow, a nonlinear temperature rise without gas flow control gives comparable results and saves substantial equipment costs and the care necessary to maintain conditions.

#### ACKNOWLEDGMENT

The authors are indebted to Roslyn E. Kramer for her contributions to the laboratory work.

#### LITERATURE CITED

- (1) Amberg, C. H., *Can. J. Chem.* 36, 590 (1958).
- (2) Ashbury, G. K., Davies, A. T., Drinkwater, J. W., *ANAL. CHEM.* 29, 918 (1957).
- (3) Brenner, N., O'Brien, L., Coates, V., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1958.
- (4) Dal Nogare, S., Bennett, C. E., *ANAL. CHEM.* 30, 1157 (1958).
- (5) Desty, D. H., Harbourn, C. L. A., "Vapour Phase Chromatography," Butterworth Scientific Publications, London, 1957.
- (6) Drew, C. M., McNesby, J. R., Smith, S. R., Gordon, A. S., *ANAL. CHEM.* 28, (1956).
- (7) Harrison, G. F., Knight, P., Kelly, R. P., Heath, M. T., Second International Symposium on Gas Chromatography, Amsterdam, May 1958.

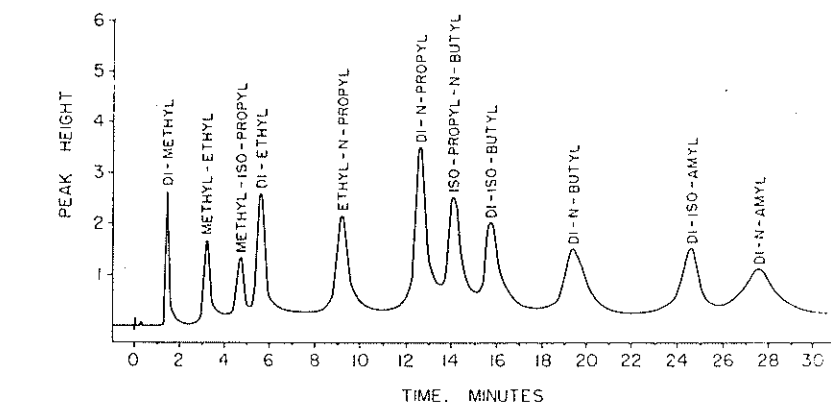


Figure 2. Nonlinear temperature programmed separation of a homologous series of sulfides

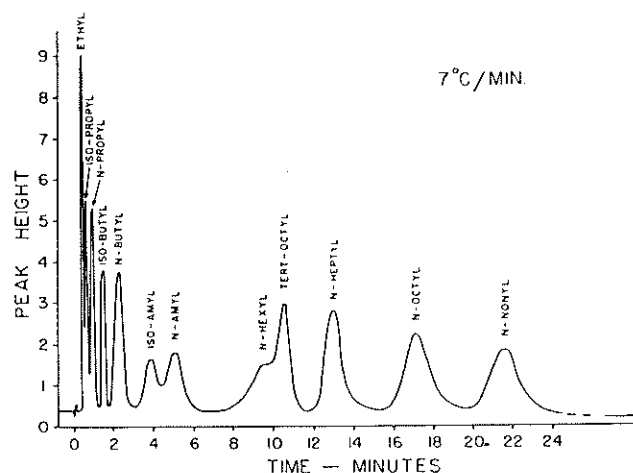


Figure 3. Linear temperature programmed separation of a homologous series of mercaptans

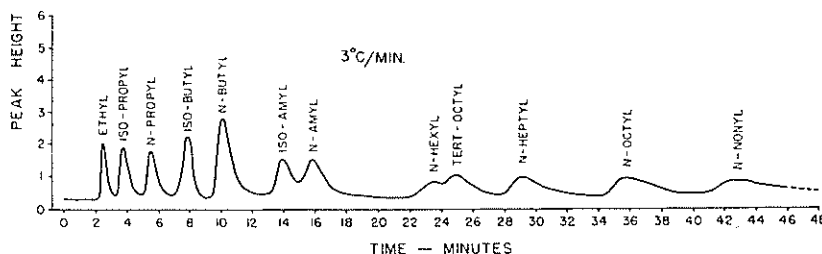


Figure 4. Linear temperature programmed separation of a homologous series of mercaptans

- (8) Keulemans, A. I. M., "Gas Chromatography," Reinhold, New York, 1957.
- (9) Mitchell, J., Jr., et al., "Organic Analysis," Vol. I, Interscience, New York, 1954.
- (10) Phillips, C., "Gas Chromatography," Academic Press, New York, 1956.
- (11) Ryce, S. A., Bryce, W. A., *ANAL. CHEM.* 29, 925 (1957).
- (12) Spencer, C. F., Baumann, F., Johnson, J. F., *Ibid.*, 30, 1473 (1958).

RECEIVED for review November 12, 1958.  
Accepted July 23, 1959.